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Optimum charge-carrier mobility for a polymer light-emitting diode

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The performance of polymer light-emitting diodes (PLEDs) consisting of various poly-p(phenylene vinylene) (PPV)-based derivatives has been investigated. It is demonstrated that an increased charge carrier mobility gives rise to an enhancement of the quenching of the electroluminescence at the metallic cathode. As a result the power efficiency of PPV-based LEDs under operating conditions exhibits a distinct optimum at a mobility of about 10^{-11} m^2/V s. © *2000 American Institute of Physics.* [S0003-6951(00)04639-8]

Since the discovery of electroluminescence in conjugated polymers[1] it has been recognized that charge transport is a key ingredient for the efficiency of polymer light-emitting diodes (PLEDs).[2,3] From temperature dependent current–density–voltage ($J-V$) characteristics it has been obtained that the hole transport in poly(dialkoxy-p-phenylene vinylene), or dialkoxy-PPV, is governed by a combination of space charge effects and a field- and temperature-dependent mobility.[4] The electron conduction in the PPV-derivatives proved smaller than the hole conduction, which was attributed to the presence of traps[5] or lower electron mobility.[6]

For PLEDs, in which both electrons and holes are injected, the different conduction of electrons and holes is directly responsible for the distribution of light output in the polymer layer. Model calculations of a PLED with Ohmic contacts[7,8] or tunneling contacts[8] showed that the light output is mainly confined in a region close to the cathode, due to the reduced electron conduction. As a result nonradiative energy transfer to the metallic cathode strongly reduces the quantum efficiency (QE) (photon/charge carrier) of the PLED at low voltages. At higher voltages the difference between electron and hole transport decreases[5,6] and the recombination zone shifts away from the interface. The resulting reduction in nonradiative recombination losses at the cathode gives rise to an increase of the QE, as shown in Fig. 1 for a single-layer dialkoxy-PPV (OC_1C_{10}) LED with a thickness of 200 nm. Using our PLED device model[7] for the present device agreement with the experiment is obtained using a quenching region L_q of 8 nm.

The mechanism for the nonradiative energy transfer to the metallic electrode is dependent on the distance of an excited molecule to the metal. For large distances the interaction of an oscillating dipole with its image dipole dominate. For small distances ($\leqslant 5$ nm) scattering by the metal surface is relevant.[9] From photoluminescent (PL) experiments an effective quenching region of nearly 20 nm has been obtained for cyano derivatives of PPV.[10] In order to further demonstrate the effect of such a quenching region the calculated QE for various L_q has been included in Fig. 1. It appears that an increase of L_q gives rise to two effects: The maximum QE decreases with increasing L_q and the maximum QE is reached at higher voltages. The reduction of the maximum QE is due to the fact that for larger L_q a larger part of the device is not active in the light-emission process. The slower increase of QE with V directly results from the fact that for larger L_q a shift of the recombination zone out of the broader quenching region requires larger voltages.

In a PLED the recombination strength between the electrons and holes is of the Langevin type.[11,12] As a result both light output and current are proportional to the charge carrier mobility. Consequently, the QE of a PLED, which represents light-output/current, is expected to be independent of the mobility. However, with increasing mobility the voltage required to maintain a certain amount of light-output (or cur-

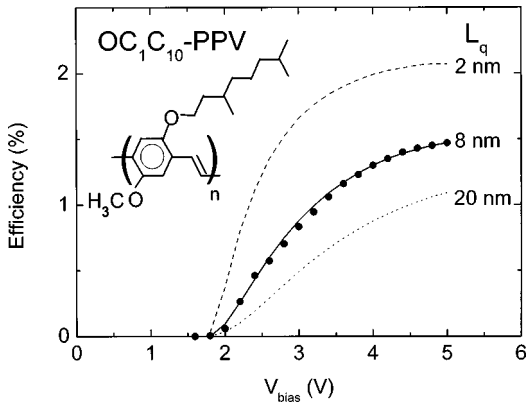

FIG. 1. Experimental QE-V characteristic (symbols) for the OC_1C_{10}-based LED together with model calculations for various lengths of the quenching region at the cathode. Agreement with experiment is obtained for $L_q = 8$ nm. In the inset the structure of the OC_1C_{10}-PPV is shown.

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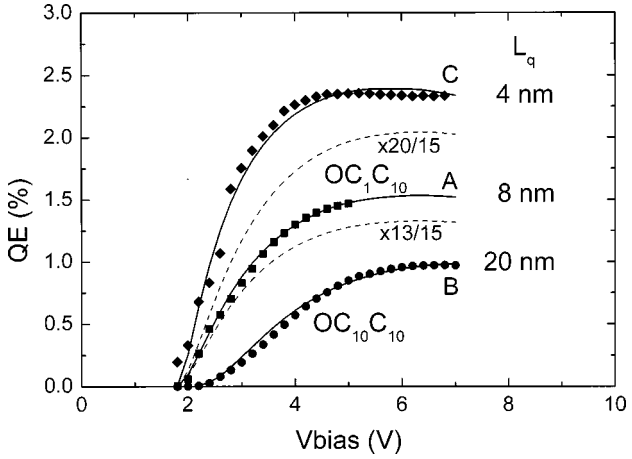

FIG. 2. Quantum efficiency (photons/charge carrier) QE as a function of applied voltage for PLEDs of polymers A, B, and C from experiment (symbols) and model (lines) with thickness $L=200$ nm. The dashed lines represent the predictions for polymers B and C using a quenching width of 8 nm, as obtained for polymer A. The observed difference between experiment and prediction in both the rise of QE with V and maximum attainable QE of polymers B (high mobility) and C (low mobility) is simultaneously explained by a change of L_q to 20 and 4 nm, respectively, as shown by the solid lines.

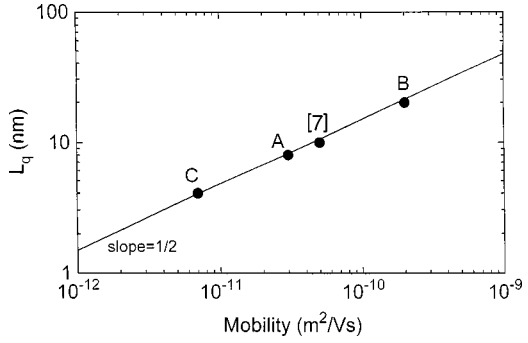

FIG. 3. Observed quenching width L_q as a function of the carrier mobility μ for the polymers considered in this study. The solid line with slope=0.5 indicates that the dependence of L_q on μ can be approximated by a square-root dependence.

rent) will decrease, and as a result an enhanced mobility is expected to increase the power efficiency $PE=L/J\times V$.[7] In a recent study[13] the hole mobility of various PPV-derivatives with different chemical side chains has been investigated. It appeared that the presence of two bulky $OC_{10}H_{21}$ side chains ($OC_{10}C_{10}$-PPV) gives rise to an increase of the hole mobility of one order of magnitude with regard to the OC_1C_{10}-PPV, due to a reduction of the energetic disorder. Since the PL efficiency of the $OC_{10}C_{10}$-PPV (13%), in spite of the higher mobility, is nearly equal to the PL efficiency of the OC_1C_{10} (15%), this material is a promising candidate for further improvement of the performance of PPV-based PLEDs.

In this study the device performance of three different dialkoxy-PPV based polymers is compared: OC_1C_{10}(A),[7] $OC_{10}C_{10}$(B),[13] and a random copolymer of OC_1C_{10} and 2,5-bischloromethyl-4-methoxy-1-(3,7-dimethyloctyloxy)-benzene (C),[14] with charge carrier mobilities of 3×10^{-11}, 2×10^{-10}, and $7\times10^{-12}\,m^2/V\,s$, respectively. The structure of polymer A is indicated in Fig. 1, the structure of polymers B and C can be found in Refs. 13 and 14. The PL efficiency of polymers A, B, and C amount to 15%, 13%, and 20%, respectively. The devices under investigation consist of a patterned indium–tin–oxide (ITO) anode on top of a glass substrate, the spin coated PPV derivative as the active layer, and a low work function metal (Ca) cathode. The thickness of the polymer layers amounts to 200 nm, as measured by a Dektak 3030 surface profiler. The $J-V$ and $L-V$ measurements are performed in nitrogen atmosphere. In Fig. 2 the quantum efficiency QE is shown for the three different polymers. As shown in Fig. 1 for polymer A(OC_1C_{10}) we obtain that the bias dependence of QE is well described by taking into account a quenching region of 8 nm at the cathode. In prior experiments[7] on a different batch of OC_1C_{10}, with a somewhat higher carrier mobility of $5\times10^{-11}\,m^2/V\,s$ (as compared to the $3\times10^{-11}\,m^2/V\,s$ of polymer (A) a slightly larger L_q of 10 nm had been obtained. As stated above, for polymers B and C it is expected that the QE is unaffected by the charge carrier mobility. Thus, in order to predict the voltage dependence of QE for these polymers we expect that we only have to correct the calculated QE of polymer A for the different PL efficiencies of polymers B and C, as is indicated (dashed lines) in Fig. 2.

Experimentally, however, it appears that the maximum QE of polymer B with the highest carrier mobility ($OC_{10}C_{10}$) of 1.0% is significantly lower than the predicted value of 1.35% (lower dashed line) of polymer B. Furthermore, for polymer B the maximum QE is only reached at 7 V in contrast to the 5.5 V of polymer A. For polymer C, with the lowest carrier mobility, on the other hand the maximum experimental QE of 2.4% is larger than the expected value of 2.0% (upper dashed line). Also, for this polymer the experimental maximum QE is already reached at 4.5 V instead of the expected 5.5 V. In our device model the only parameter which influences both the maximum QE as well as the rise of the QE with V is the width of the quenching region L_q, as shown in Fig. 1. For the high mobility polymer B, increasing L_q from 8 to 20 nm in our model leads to a simultaneous agreement of both the rise of QE with V and the maximum value of QE. For the low mobility polymer C a reduction of L_q from 8 to 4 nm again gives rise to a close agreement of the rise of QE with V as well as the maximum value of QE. Thus our earlier expectation that the QE of a PLED is not affected by the mobility is proven not to be correct.

The experimental results together with our device modeling clearly indicate that the width of the quenching region L_q increases with increasing charge carrier mobility. In Fig. 3 we plotted L_q as a function of the mobility of the three polymers studied here as well as our earlier result[7] on a different $OC_{10}C_{10}$ batch. From these data points it appears that the L_q dependence on the mobility can be approximated by a square-root dependence. If quenching the electroluminescence at the metallic electrode is dominated by exciton diffusion, L_q is described by $\sqrt{(D_e\tau)}$, with D_e the diffusion constant and τ the lifetime of the excitons. In order to obtain a $L_q\sim\sqrt{\mu_p}$ dependence we then have to assume that D_e is in first order proportional to the charge carrier mobility μ_p. However, the fact that nonradiative energy transfer to the cathode also occurs when the polymer is separated from the metal by a spacer layer [10] makes the dominance of exciton diffusion in the EL quenching questionable. Furthermore, a proportionality between μ_p, governed by hopping in a Gaussian broadened DOS, and D_e, which is expected to be

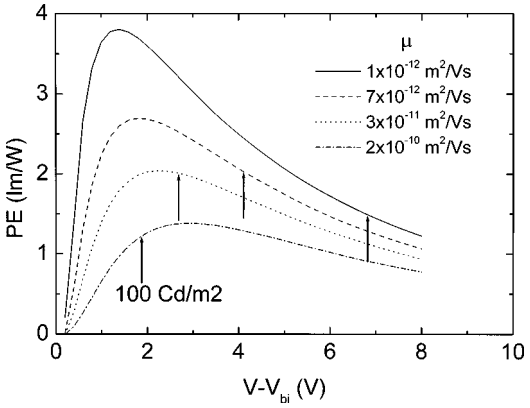

FIG. 4. Calculated power efficiency PE as a function of applied voltage V, which corresponds to an effective voltage of $V-V_{\mathrm{bi}}$ with V_{bi} the built-in voltage for PLEDs with different charge carrier mobilities. The arrows indicate the voltage for which the light output is equal to 100 cd/m^2, a value which is typical for applications. For this light-output the polymer with a mobility of 7×10^{-12} m^2/V s exhibits the highest power efficiency.

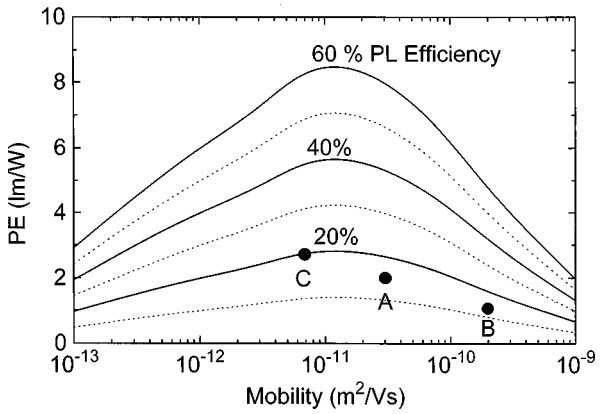

FIG. 5. Calculated map of the power efficiency PE at 100 cd/m^2 for orange emitting polymers as a function of the charge carrier mobility μ and PL efficiency. The polymers A, B, and C are indicated by symbols. Using this map the performance of a polymer with known μ and PL efficiency can be directly evaluated.

of the Förster type,[15,16] is not obvious. A deeper understanding of the exact coupling between EL quenching and charge transport will be the subject of further study. Here, we focus on the relevance of such a coupling for the performance of a PLED.

Taking into account the enhanced quenching near the cathode for higher μ_p the PE for polymers with various mobilities are calculated, as shown in Fig. 4. In this calculation a PL efficiency of 20% is used, independent of the mobility. It is demonstrated that due to the reduced quenching the PE as a function of voltage is larger for lower mobility. However, for applications the power efficiency at a light output of 100 cd/m^2 is relevant, and the voltage for which this light output is obtained is indicated by the arrows in Fig. 4. The 100 cd/m^2 point for a low mobility of only 1×10^{-12} m^2/V s is reached at a high voltage of about 7 V, which leads to an expected reduction of PE. For a mobility of 2×10^{-10} m^2/V s the 100 cd/m^2 point is already reached at 1.9 V, but the enhanced quenching also reduces the PE. As a result the polymer with a mobility of 7×10^{-12} m^2/V s (C) has the highest power efficiency of 2 lm/W at the 100 cd/m^2 point. By performing these calculations for a large series of mobilities and PL efficiencies we are now able to map the PLED performance of the various polymers as shown in Fig. 5, which is the main result of our study. In Fig. 5 it is demonstrated that the optimum charge carrier mobility at a given PL efficiency amounts to 1×10^{-11} m^2/V s. It should be noted that a reduced charge carrier mobility is usually accompanied with an increase of the PL efficiency, since it becomes more difficult for excitons to diffuse to a nonradiative center in the polymer. As seen in Fig. 5, a polymer with a charge carrier mobility of only 1×10^{-13} m^2/V s requires a PL efficiency of 50% in order to compete with the performance of polymer C. For polymers with mobilities larger than 1×10^{-11} m^2/V s on the other hand, only an increase in performance is expected when the recombination zone is separated from the cathode (e.g., by using a two layer device), which would eliminate the enhanced quenching of the electroluminescence.

In conclusion, we have studied the relevance of the charge carrier mobility on the device performance of PPV-based PLEDs. An increase of the charge carrier mobility is accompanied by an enhancement of the width of the exciton quenching region close to the metallic cathode. The resulting decrease of the quantum efficiency gives rise to a reduction of the power efficiency and to a distinct optimum for the charge carrier mobility.

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